Electronic Supplementary Information

Highly Photostable Luminescent Open-shell (3,5-Dihalo-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl Radicals: Significant Effects of Halogen Atoms on Their Photophysical and Photochemical Properties

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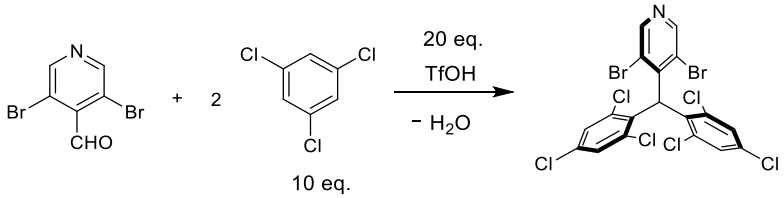
Contents

Materials

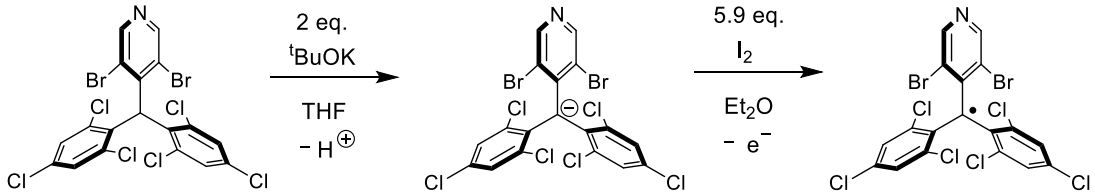
3,5-Dibromo-4-pyridinecarboxaldehyde, 3,5-difluoro-4-formylpyridine, ^{t}BuOK in THF (1M solution), and 4-hydroxy-TEMPO were purchased from Sigma-Aldrich Co.LLC., 1,3,5-trichlorobenzene was from Wako Pure Chemical Industries, Ltd., trifluoromethanesulfonic acid was from Tokyo Chemical Industry Co., Ltd.

Synthesis of (3,5-dibromo-4-pyridyl)bis(2,4,6-trichlorophenyl)methane (α*H*-Br$_2$PyBTM)



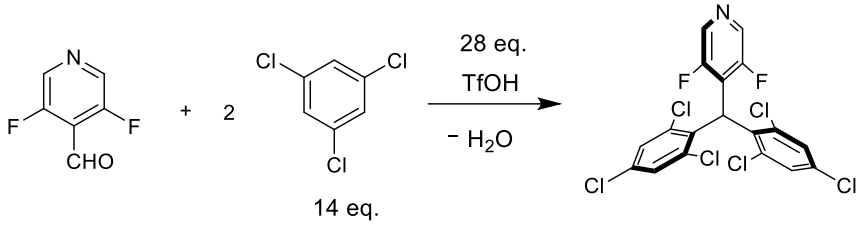
α*H*-Br$_2$PyBTM was synthesized by similar method to that of α*H*-PyBTM[1] utilizing superacid-catalyzed condensation of pyridine carboxaldehyde with arenes.[2] Under a nitrogen atmosphere, 3,5-dibromo-4-pyridinecarboxaldehyde (532 mg, 2.01 mmol, 1 eq.) and 1,3,5-trichlorobenzene (3.64 g, 20.1 mmol, 10 eq.) was heated to 180 °C. Trifluoromethanesulfonic acid (6.0 g, 40 mmol, 20 eq.) was added, and the reaction mixture was stirred for 9.5 hours at 180 °C. The reaction mixture was cooled to r.t., dissolved in CH_2Cl_2, and added to ice water. The mixture was neutralized using $NaHCO_3$ aq, extracted with CH_2Cl_2 (3 × 50 mL), washed with $NaHCO_3$ aq, and dried by $MgSO_4$. The organic layer was purified by SiO_2 column chromatography (CH_2Cl_2 : hexane = 1:1), evaporated, and dried in vacuo to afford α*H*-Br$_2$PyBTM (279 mg, 0.458 mmol, 28%) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.64 (s, 1H), 8.54 (s, 1H), 7.39 (dd, J = 2.1 Hz, 2.2 Hz, 2H), 7.26 (d, 1H), 7.24 (d, J = 2.3 Hz, 1H), 6.62 (s, 1H). **MS** (positive ion mode FAB) m/z: $[M+H]^+$ Calcd for $C_{18}H_8Br_2Cl_6N$ 609.71; Found 610. **Elem. Anal.** Calcd for $C_{18}H_7NBr_2Cl_6$: C 35.46, H 1.16, N 2.30. Found, C 35.48, H 1.22, N 2.20.

Synthesis of (3,5-dibromo-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl radical (Br$_2$PyBTM)



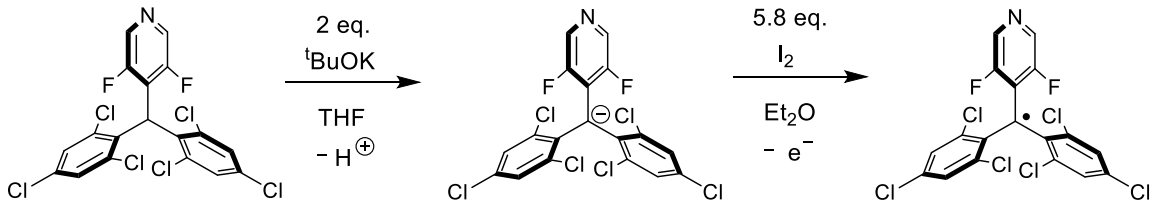
Br$_2$PyBTM was synthesized by similar method to that of PyBTM.[1] Under a nitrogen atmosphere, α*H*-Br$_2$PyBTM (152 mg, 0.249 mmol) was dissolved in dry THF (11 mL). ^{t}BuOK in THF (1M solution, 0.5 mL, 2 eq.) was added dropwise and the color of the solution changed to red. The reaction mixture was stirred overnight in the dark. I_2 (373 mg, 1.47 mmol, 5.9 eq.) in dry Et_2O (50 mL) was added dropwise and stirred for 2.25 h. Remaining I_2 was reduced by washing with 10 % $Na_2S_2O_3$ aq 3 times, water layer was extracted with Et_2O, and combined organic layer was dried with $MgSO_4$. The red solution was filtered, evaporated, purified by Al_2O_3 column chromatography (Et_2O : hexane = 1:4) and dried in vacuo to afford Br$_2$PyBTM (70.4 mg, 0.116 mmol, 46%) as a red solid. **IR** (KBr) 3092 (w), 3048 (w), 2955 (w), 2923 (w), 1553 (s), 1527 (s), 1395 (s), 1373 (s), 1292 (m), 1216 (w), 1204 (w), 1182 (m), 1134 (m), 1084 (w), 1071 (w), 1053 (w), 925 (w), 884 (w), 860 (s), 829 (m), 808 (s), 791 (m), 753 (m), 726 (w), 661 (w), 567 (w), 539 (w) **HRMS** (negative ion mode ESI-TOF) m/z: $[M]^-$ Calcd for $C_{18}H_6Br_2Cl_6N$ 607.6948; Found 607.6945. **Elem. Anal.** Calcd for $C_{18}H_6NBr_2Cl_6$: C 35.51, H 0.99, N 2.30. Found, C 35.83, H 1.20, N 2.07. **ESR** Spin concentration of Br$_2$PyBTM in toluene (1.00×10^{-4} M) was estimated by comparing the value of twice-integration of the signal intensity with that of the reference sample (4-hydroxy-TEMPO in toluene; 9.8×10^{-5} M). The existence of S = 1/2 spin on one Br$_2$PyBTM molecule was confirmed.

Synthesis of (3,5-difluoro-4-pyridyl)bis(2,4,6-trichlorophenyl)methane (α*H*-F_2PyBTM)



α*H*-F_2PyBTM was synthesized by similar method to that of α*H*-PyBTM[1] utilizing superacid-catalyzed condensation of pyridine carboxaldehyde with arenes.[2] Under a nitrogen atmosphere, 3,5-difuoro-4-formylpyridin (104 mg, 0.727 mmol, 1 eq.) and 1,3,5-trichlorobenzene (1.81 g, 10.0 mmol, 14 eq.) was heated to 180 °C. Trifluoromethanesulfonic acid (3.0 g, 20 mmol, 28 eq.) was added, and the reaction mixture was stirred for 9 hours at 180 °C. The reaction mixture was cooled to r.t., dissolved in CH_2Cl_2, and added to ice water. The mixture was neutralized to pH 7 using $NaHCO_3$ aq, extracted with CH_2Cl_2 (3 × 50 mL), washed with $NaHCO_3$ aq, and dried by $MgSO_4$. The organic layer was purified by SiO_2 column chromatography (CH_2Cl_2 : hexane = 1:1), evaporated, and dried in vacuo to afford α*H*-F_2PyBTM (231 mg, 0.458 mmol, 65%) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.33 (s, 1H), 8.21 (s, 1H), 7.33 (s, 4H), 6.64 (s, 1H). **MS** (positive ion mode FAB) m/z: $[M-H]^+$ Calcd for $C_{18}H_8Cl_6F_2N$ 487.87; Found 488. **Elem. Anal.** Calcd for $C_{18}H_7NCl_6F_2$: C 44.31, H 1.45, N 2.87. Found, C 44.45, H 1.67, N 2.78.

Synthesis of (3,5-difluoro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl radical (F_2PyBTM)



F_2PyBTM was synthesized by similar method to that of PyBTM.[1] Under a nitrogen atmosphere, α*H*-F_2PyBTM (121 mg, 0.248 mmol) was dissolved in dry THF (13 mL). ^{t}BuOK in THF (1M solution, 0.5 mL, 2 eq.) was added dropwise and the color of the solution changed to reddish orange. The reaction mixture was stirred overnight in the dark. I_2 (367 mg, 1.45 mmol, 5.8 eq.) in dry Et_2O (43 mL) was added dropwise and stirred for 2.25 h. Remaining I_2 was reduced by washing with 10 % $Na_2S_2O_3$ aq 3 times, water layer was extracted with Et_2O, and combined organic layer was dried with $MgSO_4$. The reddish orange solution was filtered, evaporated, purified by Al_2O_3 column chromatography (Et_2O : hexane = 1:4) and dried in vacuo to afford F_2PyBTM (54.3 mg, 0.112 mmol, 45%) as a red solid. **IR** (KBr) 3049 (w), 2955 (w), 2923 (w), 2851 (w), 1558 (s), 1529 (s), 1423 (s), 1372 (s), 1286 (m), 1257 (m), 1220 (m), 1185 (m), 1142 (m), 1028 (s), 918 (m), 875 (w), 859 (s), 829 (m), 806 (m), 793 (m), 734 (w), 570 (m), 538 (w) **HRMS** (negative ion mode ESI-TOF) m/z: $[M]^-$ Calcd for $C_{18}H_6Cl_6F_2N$ 485.8571; Found 485.8555. **Elem. Anal.** Calcd for $C_{18}H_6NCl_6F_2$: C 44.40, H 1.24, N 2.88. Found, C 44.79, H 1.63, N 2.67. **ESR** Spin concentration of F_2PyBTM in toluene (1.03×10^{-4} M) was estimated by comparing the value of twice-integration of the signal intensity with that of the reference sample (4-hydroxy-TEMPO in toluene; 9.8×10^{-5} M). The existence of S = 1/2 spin on one F_2PyBTM molecule was confirmed.

X-ray structural analysis

Red single crystals of Br_2PyBTM and F_2PyBTM were obtained by diffusing water (the lower layer) into an acetone solution of Br_2BTM or F_2PyBTM (the upper layer). Diffraction data for X-ray analysis were collected with an AFC10 diffractometer coupled with a Rigaku Saturn CCD system equipped with a rotating-anode X-ray generator producing graphite-monochromated MoKα radiation (λ = 0.7107 Å). Lorentz polarization and numerical absorption

corrections were performed with the program *Crystal Clear 1.3.6.* Structures were solved by the direct method using SIR 92 software[3] and refined against F2 using SHELXL-97.[4] Br_2PyBTM was refined using ISOR restraints. *Crystal Structure 4.0* software was used to prepare the material for publication. The crystallographic data are listed in Table S1. CCDC 1058942 and 1058943 contain the supplementary crystallographic data of this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Instruments

^{1}H NMR spectra were recorded using a BRUKER US500. The reported chemical shifts of the solvent residual peaks were used for calibration of the ^{1}H NMR spectra in $CDCl_3$ (δ 7.26). FAB mass spectra were recorded using a JEOL JMS-700MStation mass spectrometer using 3-nitrobenzyl alcohol as a matrix, and ESI–TOF mass spectra were recorded using an LCT Micromass spectrometer. ESR spectra were recorded with a JEOL JES-FA200 spectrometer with X-band microwave. 4-Hydroxy-TEMPO was used as a spin concentration standard. Deoxygenated sample solutions were charged in a 5mmϕ sample tube. Magnetic field was calibrated with the Mn^{2+}/MnO standard. UV-vis absorption spectra were recorded with a JASCO V-570 spectrometer. Steady-state emission spectra were measured with a HITACHI F-4500 spectrometer. Sample solutions were bubbled with argon before measurement. Absolute PL quantum yields were measured with a Hamamatsu Photonics C9920-02G. Fluorescence lifetime measurements were performed using a Hamamatsu Photonics Quantaurus-Tau C11367-02. Temperature dependence of fluorescence and UV-vis spectra were measured with a temperature controller (UNISOKU USP-203A). Electrochemical measurements were recorded with an ALS 750D electrochemical analyzer (BAS. Co., Ltd.). The working electrode was a 0.3 mm o.d. glassy carbon electrode; a platinum wire served as auxiliary electrode, and the reference electrode was an Ag^+/Ag electrode (a silver wire immersed in 0.1 M Bu_4NClO_4/0.01 M $AgClO_4$/CH_3CN). Ferrocene was used as an internal standard for calibrating potentials. The solutions were deoxygenated with pure argon prior to the electrochemical measurements.

Evaluation of stability of X_2PyBTM under UV light

A solution (ca. 1×10^{-5} M, 2 mL) in 1-cm-optical-path-length quartz cells was bubbled with argon, sealed, and set at a HITACHI F-4500 spectrometer. Intensity of luminescence at 570 nm was observed exciting at 370 nm light (excitation slit was 5.0 nm, and shutter control was off). Logarithm of fluorescence intensity versus time was plotted and a slope of approximate line was estimated to be a rate of photolysis.

Evaluation of pK_a value of X_2PyBTMH$^+$

In acetonitrile solution, pK_a of X_2PyBTMH$^+$ was evaluated using a method and references developed by Leito et al..[5] Br_2PyBTM solution was titrated with two reference bases, 3-nitroaniline: acid dissociation constant of conjugate acid pK_a = 7.68, 2-chloropyridine: pK_a = 6.79. From spectral simulation of each titration experiment, ΔpK_a (pK_a (PyBTM)−pK_a (reference base)) was calculated to be −0.59 ± 0.05, +0.36 ± 0.05 respectively, and pK_a of Br_2PyBTMH$^+$ was decided to be 7.1. F_2PyBTM solution was titrated with two reference bases, 2-chloropyridine: pK_a = 6.79, and 4-nitroaniline: pK_a = 6.22. From spectral simulation of each titration experiment, ΔpK_a (pK_a (PyBTM)−pK_a (reference base)) was calculated to be +0.19 ± 0.05, +0.46 ± 0.05 respectively, and pK_a of PyBTMH$^+$ was decided to be 6.8.

Computational details

DFT calculations were executed using the Gaussian09 program package.[6] The geometries of the compounds were optimized without symmetry constraints using the crystal structure coordinate as the starting structure. Calculations were performed using the unrestricted Becke three-parameter hybrid functional with Lee–Yang–Parr correlation functional (B3LYP)[7] or M06 functional[8] with the 6-31G(d) basis set. Cartesian coordinates of all the optimized

geometries are listed in the supporting information. Frequency calculations were carried out to ensure that the optimized geometries were minima on the potential energy surface, in which no imaginary frequencies were observed in any of the compounds. TDDFT calculations were performed using UB3LYP to calculate the first 15 doublet transitions.

Acknowledgement

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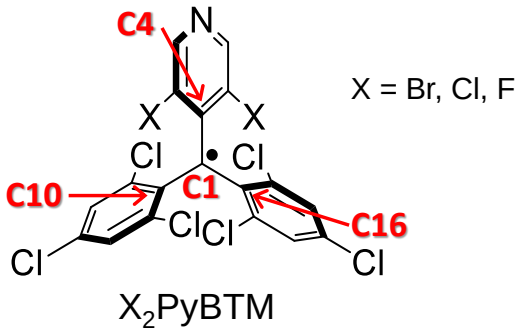
Table S1. Crystallographic data of Br_2PyBTM and F_2PyBTM.

	Br_2PyBTM	F_2PyBTM
Empirical formula	C_{18} H_6 Br_2 Cl_6 N	C_{18} H_6 Cl_6 F_2 N
Fw / g mol^{-1}	608.78	486.97
Crystal system	triclinic	monoclinic
Space group	*P*-1	$P2_1/c$
Crystal size / mm	0.35×0.15×0.10	0.65×0.45×0.25
Temperature / K	113	113
a / Å	7.461(4)	14.5687(14)
b / Å	10.846(6)	8.1370(5)
c / Å	12.660(7)	16.2873(16)
α / º	81.516(11)	90
β / º	88.763(14)	105.775 (4)
γ / º	87.731(14)	90
V / Å^3	1012.4 (9)	1858.1 (3)
Z	2	4
ρ_{calced} / g cm^{-3}	1.997	1.741
λ / Å	0.7107	0.7107
μ / mm^{-1}	4.811	0.946
Reflections collected	6357	12867
Independent reflections	3547	4067
Parameters	245	244
R_{int}	0.0591	0.0225
[a]*R*1	0.1517	0.0434
[b]*wR*2	0.4232	0.1000
[c]GoF	1.173	1.058
CCDC No.	1058943	1058942

[a] $R_1 = \Sigma||F^o|-|F^c||/\Sigma|F^o|$ ($I>2\sigma(I)$). [b] $wR_2 = [\Sigma(w(F^{o2}-F^{c2})^2/\Sigma w(F^{o2})^2]^{1/2}$ ($I>2\sigma(I)$). [c] GoF = $[\Sigma(w(F^{o2}-F^{c2})^2/\Sigma(N^r-N^p)^2]$

Table S2. Selected angles in the crystal of Br_2PyBTM and F_2PyBTM



Angles	Cl_2PyBTM	Br_2PyBTM	F_2PyBTM
C4C1C10	117.5(4)° [a]	118.8(18)°	118.2(2)°
C4C1C16	121.0(4)° [a]	119.6(19)°	122.0(3)°
C10C1C16	121.5(4)° [a]	121.7(18)°	119.6(3)°
Dihedral angle between C4C10C16 plain and			
(3,5-dihalopyridyl)	49.3° [a]	48.1°	33.3°
(2,4,6-trichlorophenyl including C10)	49.5° [a]	42.3°	56.4°
(2,4,6-trichlorophenyl including C16)	42.6° [a]	53.6°	51.7°

[a] cited from ref. 1.

Table S3. Calculated angles of Br_2PyBTM and F_2PyBTM using UB3LYP/6-31G(d)

Angles	Cl_2PyBTM	Br_2PyBTM	F_2PyBTM
C4C1C10	119.9°	119.5°	120.0°
C4C1C16	119.9°	119.5°	120.0°
C10C1C16	120.2°	121.0°	120.0°
Dihedral angle between C4C10C16 plain and			
(3,5-dihalopyridyl)	47.5°	52.7°	31.3°
(2,4,6-trichlorophenyl including C10)	49.2°	48.5°	52.6°
(2,4,6-trichlorophenyl including C16)	49.2°	48.5°	52.6°

Table S4. Calculated angles of Br_2PyBTM and F_2PyBTM using UM06/6-31G(d)

Angles	Cl_2PyBTM	Br_2PyBTM	F_2PyBTM
C4C1C10	120.0°	119.2°	120.0°
C4C1C16	120.0°	119.2°	120.0°
C10C1C16	120.1°	121.6°	120.1°
Dihedral angle between C4C10C16 plain and			
(3,5-dihalopyridyl)	47.3°	50.1°	35.1°
(2,4,6-trichlorophenyl including C10)	49.1°	47.1°	50.6°
(2,4,6-trichlorophenyl including C16)	49.1°	47.1°	50.6°

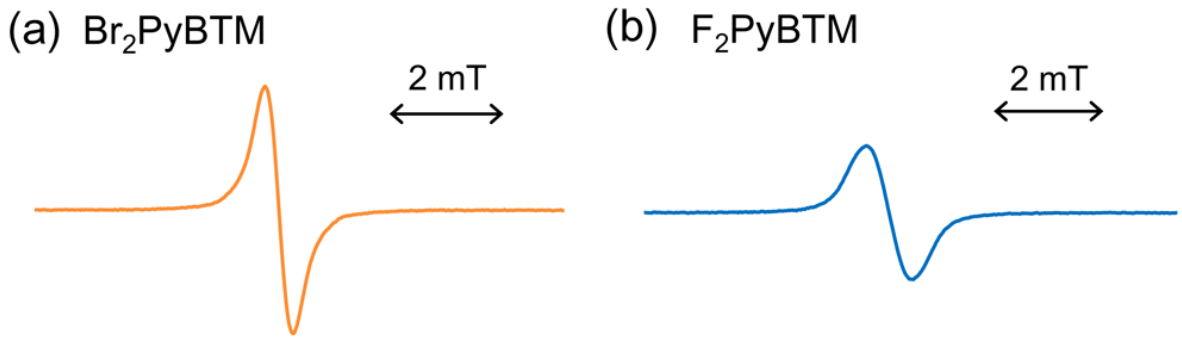


Fig. S1 ESR spectrum of (a) Br_2PyBTM and (b) F_2PyBTM in toluene at room temperature.

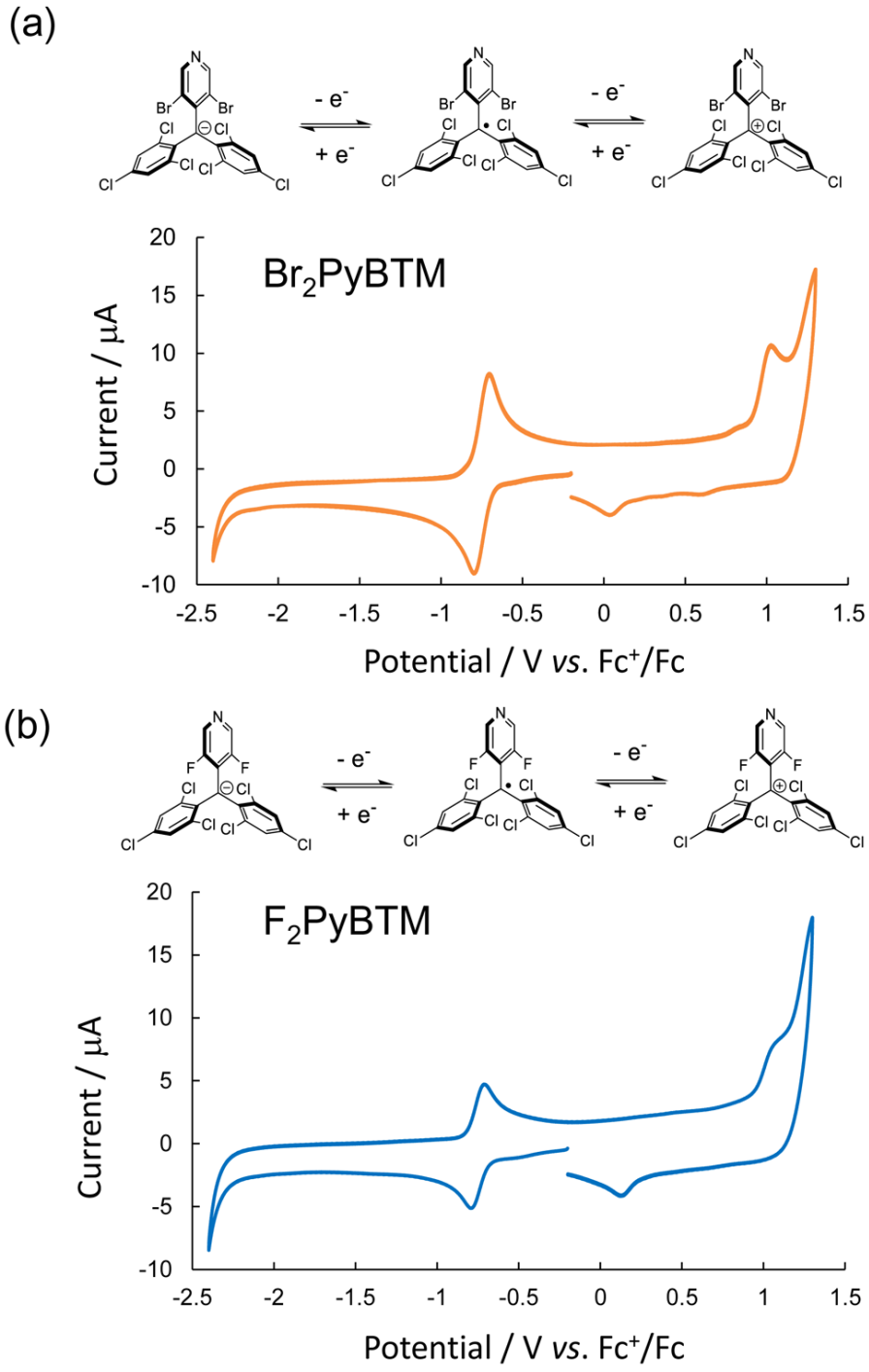


Fig. S2 Cyclic voltammograms of (a) Br_2PyBTM (0.5 mM) and (b) F_2PyBTM (0.5 mM) in 0.1 M Bu_4NClO_4–CH_2Cl_2 at a scan rate of 0.1 V s^{-1}.

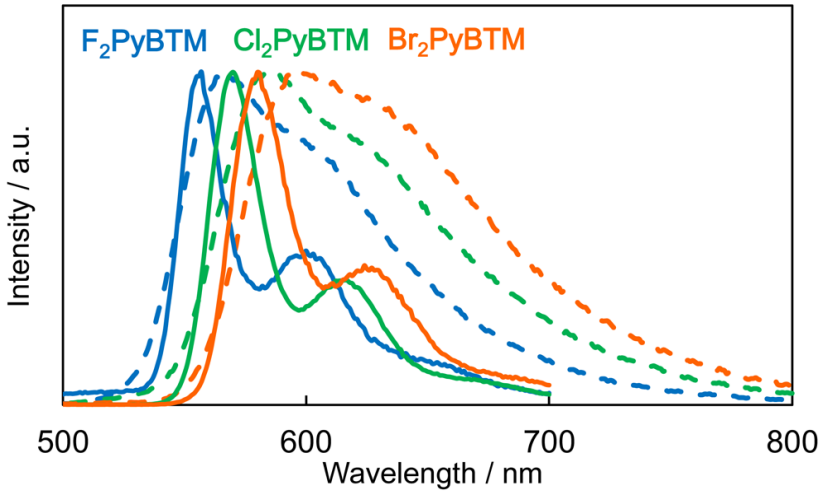


Fig. S3 Corrected emission spectra of Br_2PyBTM (orange), Cl_2PyBTM (green), and F_2PyBTM (blue) at 77 K in EPA (diethyl ether : isopentane : ethanol 5 : 5 : 2 v/v) matrix (solid lines) and at room temperature in CH_2Cl_2 (dashed lines).

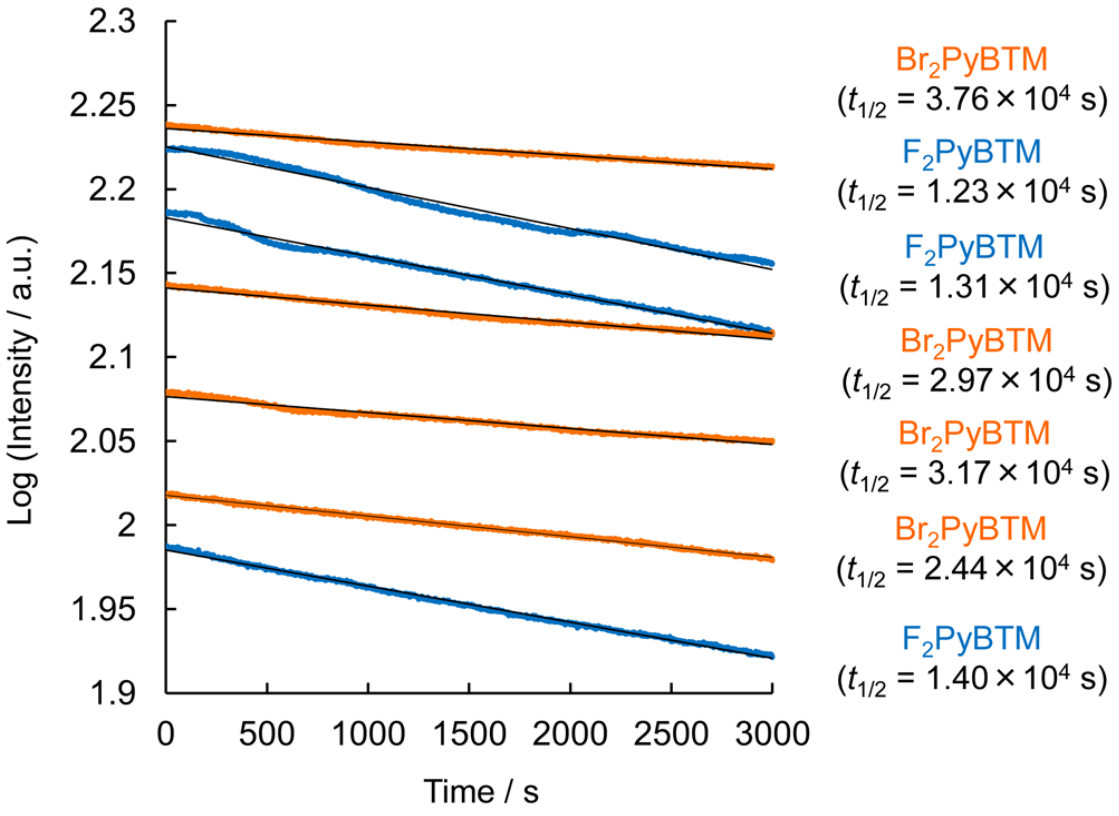


Fig. S4 Plots showing the emission decay of Br_2PyBTM (Exp. No. 3 in Table S3) and F_2PyBTM (Exp. No. 1, 2, 3, 5 in Table S3) in dichloromethane under continuous excitation with light at λ_{ex} = 370 nm. The half-lives ($t_{1/2}$) are given by linear approximation.

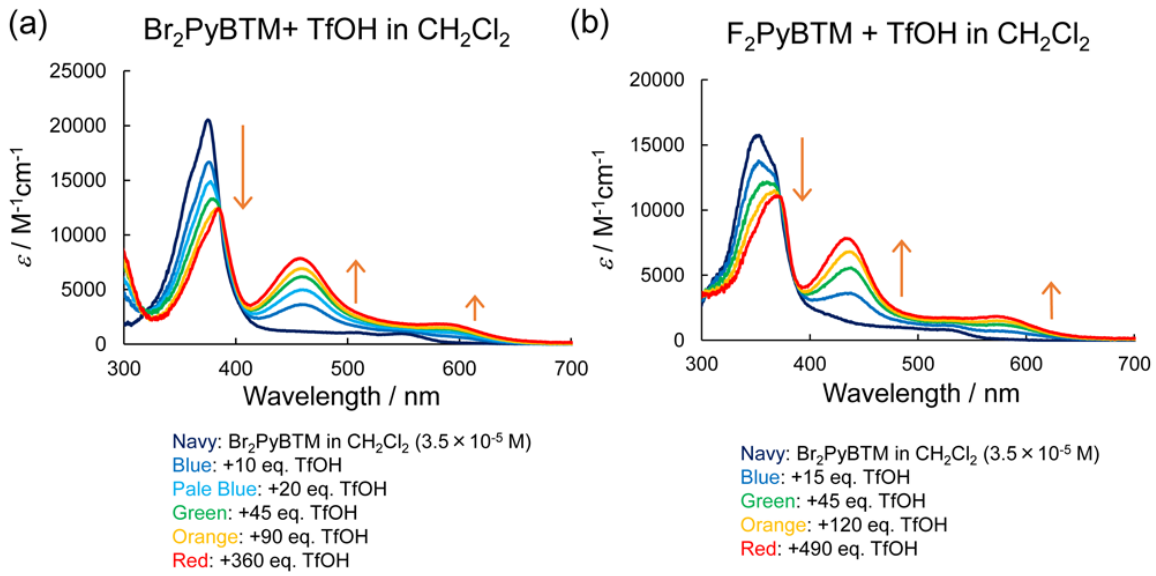


Fig. S5 Protonation of (a) Br_2PyBTM and (b) F_2PyBTM by titration with trifluoromethanesulfonic acid (TsOH) in dichloromethane.

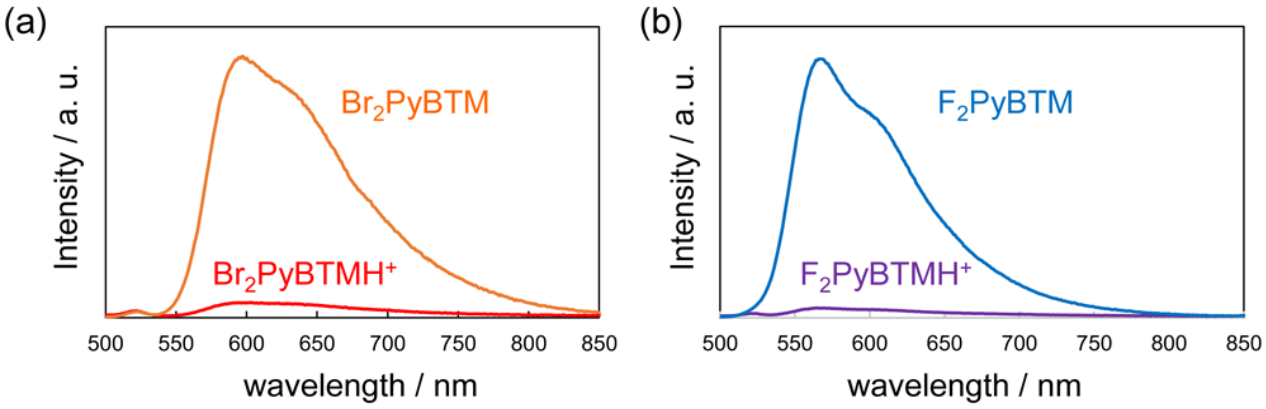


Fig. S6 Corrected fluorescence spectra of (a) Br_2PyBTM and Br_2PyBTMH$^+$, and (b) F_2PyBTM and F_2PyBTMH$^+$. Fluorescence of protonated forms are almost quenched.

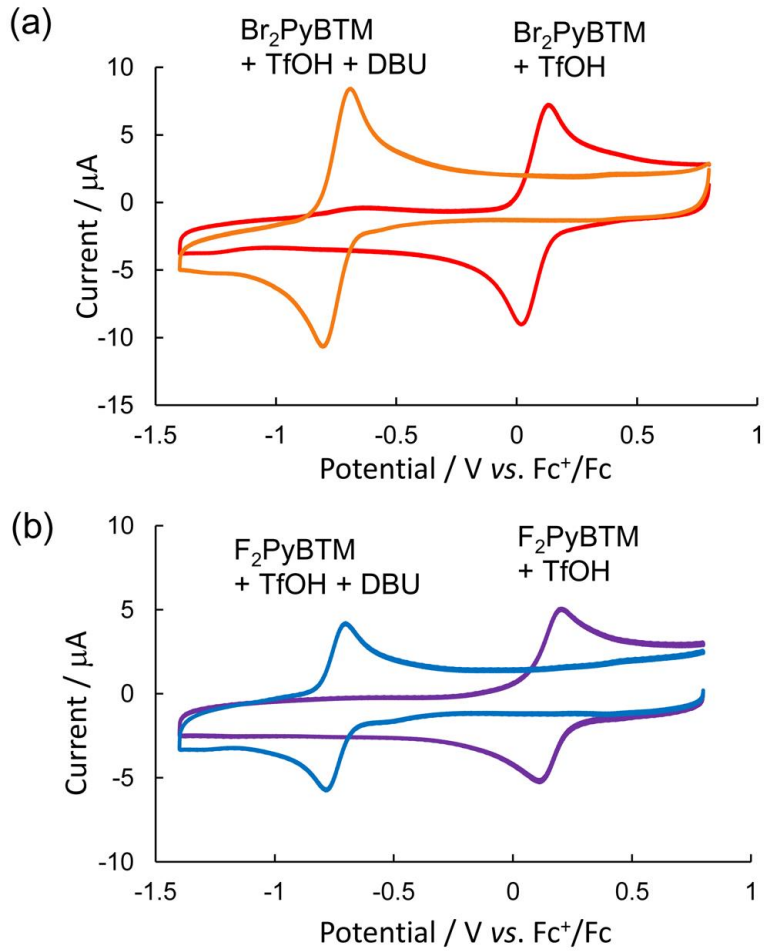


Fig. S7 (a) Proton-response of cyclic voltammograms (CVs) of Br_2PyBTM solution (0.5 mM, 5 mL) in 0.1 M Bu_4NBF_4–CH_2Cl_2 at a scan rate of 0.1 V s^{-1}. Trifluoromethanesulfonic acid (TfOH, ca. 1 eq.) was added and CV was measured (red line). Diazabicyclo[5.4.0]undec-7-ene (DBU, ca. 1.1 eq.) was added to neutralize the solution and CV was measured (orange line) to observe reversibility of protonation. (b) Proton-response of CVs of F_2PyBTM solution (0.5 mM, 5 mL) in 0.1 M Bu_4NBF_4–CH_2Cl_2 at a scan rate of 0.1 V s^{-1}. TfOH (ca. 1 eq.) was added and CV was measured (blue line). DBU (1.1 eq.) was added to neutralize the solution and CV was measured (purple line) to observe reversibility of protonation.

Cartesian coordinates of all the optimized geometries by DFT calculation

Br_2PyBTM (UB3LYP/6-31G(d))

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	-1.973816	1.580145	-2.132578
2	35	0	1.973920	1.580030	2.132565
3	17	0	0.708826	-2.101658	2.066852
4	17	0	-1.798065	0.922238	2.435697
5	17	0	-5.256946	-2.797568	0.696927
6	17	0	5.256830	-2.797637	-0.697062
7	17	0	1.797914	0.922203	-2.435679
8	17	0	-0.708749	-2.101692	-2.066723
9	7	0	0.000122	4.473365	0.000010
10	6	0	-2.877931	-2.321910	-0.530226
11	6	0	0.000012	1.619227	0.000033
12	6	0	1.674731	-1.640670	0.679202
13	6	0	-3.737275	-1.955410	0.500648
14	6	0	-2.188928	-0.270511	1.212526
15	6	0	2.877882	-2.321933	0.530212
16	6	0	-1.674756	-1.640653	-0.679154
17	6	0	-0.840394	2.388044	-0.833783
18	6	0	1.269686	-0.584810	-0.177884
19	6	0	-3.402161	-0.930116	1.378837
20	6	0	-1.269753	-0.584784	0.177919
21	6	0	0.840478	2.387999	0.833824
22	6	0	0.813382	3.780756	0.799697
23	6	0	2.188804	-0.270574	-1.212542
24	6	0	-0.813201	3.780791	-0.799664
25	6	0	3.737180	-1.955458	-0.500724
26	6	0	-0.000021	0.140377	0.000037
27	6	0	3.402035	-0.930185	-1.378905
28	1	0	-3.146369	-3.109402	-1.223260
29	1	0	3.146363	-3.109414	1.223246
30	1	0	-4.060701	-0.660527	2.195010
31	1	0	1.467201	4.349528	1.455146
32	1	0	-1.466945	4.349605	-1.455151
33	1	0	4.060532	-0.660619	-2.195119

F_2PyBTM (UB3LYP/6-31G(d))

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	-0.325697	-1.618674	2.277081
2	17	0	-2.204466	1.162210	-2.115238
3	17	0	-5.240420	-2.545411	0.313313
4	17	0	2.204336	1.161302	2.115752
5	17	0	0.325298	-1.618165	-2.277379
6	17	0	5.239768	-2.546161	-0.313637
7	9	0	-1.936817	2.124266	1.374258
8	9	0	1.937561	2.122476	-1.373932
9	7	0	0.001306	4.811506	-0.000231
10	6	0	-0.000088	0.495403	0.000170
11	6	0	-0.936619	4.118036	0.653930
12	6	0	-0.965253	2.731089	0.670588
13	6	0	0.000206	1.947564	-0.000009
14	6	0	0.966255	2.730232	-0.670704
15	6	0	0.938690	4.117214	-0.654268
16	6	0	-3.730561	-1.667197	0.225478
17	6	0	-2.714275	-1.957418	1.128563
18	6	0	-1.518312	-1.249424	1.045717
19	6	0	-1.278109	-0.244298	0.078154
20	6	0	-2.357499	0.002756	-0.807505
21	6	0	-3.563541	-0.686415	-0.747713
22	6	0	3.729993	-1.667849	-0.225582
23	6	0	3.563114	-0.687279	0.747861
24	6	0	2.357207	0.002071	0.807810
25	6	0	1.277748	-0.244638	-0.077873
26	6	0	1.517808	-1.249551	-1.045699
27	6	0	2.713680	-1.957690	-1.128746
28	1	0	-1.698886	4.672649	1.195147
29	1	0	1.701523	4.671127	-1.195417
30	1	0	-2.850543	-2.707633	1.897348
31	1	0	-4.350346	-0.470423	-1.459576
32	1	0	4.349981	-0.471608	1.459752
33	1	0	2.849829	-2.707691	-1.897768

Br_2PyBTM (UM06/6-31G(d))

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	35	0	2.103426	1.524309	1.972390
2	35	0	-2.103182	1.525086	-1.972135
3	17	0	-0.719851	-2.120698	-2.016651
4	17	0	1.701396	0.897322	-2.454081
5	17	0	5.308325	-2.644999	-0.687137
6	17	0	-5.308546	-2.644793	0.686541
7	17	0	-1.701274	0.896596	2.454677
8	17	0	0.719297	-2.122211	2.015672
9	7	0	0.000383	4.416472	0.000424
10	6	0	2.912327	-2.274211	0.512489
11	6	0	0.000022	1.577658	0.000284
12	6	0	-1.686829	-1.642259	-0.649032
13	6	0	3.761757	-1.871901	-0.507917
14	6	0	2.159260	-0.261261	-1.236284
15	6	0	-2.912633	-2.273633	-0.513136
16	6	0	1.686541	-1.642760	0.648581
17	6	0	0.892800	2.337852	0.773692
18	6	0	-1.259805	-0.604291	0.204678
19	6	0	3.393855	-0.870327	-1.394540
20	6	0	1.259747	-0.604281	-0.204588
21	6	0	-0.892612	2.338201	-0.773062
22	6	0	-0.859226	3.726356	-0.742478
23	6	0	-2.159220	-0.261613	1.236574
24	6	0	0.859779	3.726071	0.743226
25	6	0	-3.761923	-1.871748	0.507594
26	6	0	-0.000027	0.108936	0.000096
27	6	0	-3.393879	-0.870634	1.394633
28	1	0	3.208005	-3.054096	1.208694
29	1	0	-3.208588	-3.053043	-1.209785
30	1	0	4.047438	-0.580683	-2.212539
31	1	0	-1.556880	4.293997	-1.358866
32	1	0	1.557688	4.293407	1.359613
33	1	0	-4.047395	-0.581312	2.212794

F_2PyBTM (UM06/6-31G(d))

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	17	0	-0.251640	-1.686637	2.177956
2	17	0	-2.204810	1.230576	-2.036822
3	17	0	-5.198730	-2.536304	0.310295
4	17	0	2.206123	1.230942	2.035749
5	17	0	0.249678	-1.689622	-2.175408
6	17	0	5.198105	-2.537743	-0.310901
7	9	0	-1.818683	2.107352	1.497061
8	9	0	1.819746	2.106017	-1.497339
9	7	0	0.000867	4.788755	-0.000932
10	6	0	0.000129	0.496682	0.000138
11	6	0	-0.883794	4.100530	0.717621
12	6	0	-0.912031	2.717238	0.736292
13	6	0	0.000499	1.945652	-0.000094
14	6	0	0.913259	2.716555	-0.736903
15	6	0	0.885349	4.099865	-0.719071
16	6	0	-3.700959	-1.658019	0.226766
17	6	0	-2.669521	-1.982668	1.094131
18	6	0	-1.480174	-1.273278	1.012009
19	6	0	-1.267074	-0.235118	0.083960
20	6	0	-2.356742	0.043631	-0.767722
21	6	0	-3.556811	-0.645403	-0.711498
22	6	0	3.700447	-1.659324	-0.226880
23	6	0	3.557083	-0.645947	0.710694
24	6	0	2.357140	0.043251	0.767237
25	6	0	1.266801	-0.235938	-0.083543
26	6	0	1.479042	-1.275094	-1.010722
27	6	0	2.668263	-1.984669	-1.093088
28	1	0	-1.607720	4.654101	1.315546
29	1	0	1.609402	4.652895	-1.317337
30	1	0	-2.790731	-2.764964	1.838248
31	1	0	-4.359959	-0.407105	-1.403274
32	1	0	4.360754	-0.407163	1.401694
33	1	0	2.788838	-2.767649	-1.836586

Extracted results of TDDFT calculation.

Br_2PyBTM (UB3LYP/6-31G(d))

147A is SOMO.

Excited State 1: 2.128-A 2.5110 eV 493.77 nm f=0.0094 <S**2>=0.882
147A ->149A 0.14613
145B ->147B 0.32799
146B ->147B 0.91343

Excited State 2: 2.167-A 2.6641 eV 465.40 nm f=0.0252 <S**2>=0.924
147A ->149A 0.21897
145B ->147B 0.86763
146B ->147B -0.37212

Excited State 3: 2.182-A 2.7074 eV 457.94 nm f=0.0070 <S**2>=0.940
147A ->148A 0.22950
142B ->147B -0.42742
144B ->147B 0.83124

Excited State 4: 2.099-A 2.8770 eV 430.96 nm f=0.0066 <S**2>=0.851
147A ->150A -0.11018
143B ->147B 0.97324
145B ->147B 0.10526

Excited State 5: 2.139-A 2.8836 eV 429.96 nm f=0.0052 <S**2>=0.894
147A ->148A -0.19982
142B ->147B 0.80637
144B ->147B 0.50701

Excited State 6: 2.282-A 3.1009 eV 399.84 nm f=0.0000 <S**2>=1.051
147A ->149A 0.20836
141B ->147B 0.90850
141B ->148B 0.18927
145B ->147B -0.15706
145B ->148B -0.10944

Excited State 7: 2.336-A 3.1182 eV 397.61 nm f=0.0006 <S**2>=1.114
142A ->148A 0.14280
145A ->149A -0.11010
146A ->152A -0.11427
147A ->148A 0.12272

147A ->156A -0.18481
140B ->147B 0.87693
146B ->152B 0.12035

Excited State 8: 2.333-A 3.3223 eV 373.19 nm f=0.0917 <S**2>=1.111
147A ->148A 0.82691
140B ->147B -0.15233
142B ->147B 0.35176
144B ->147B -0.13839
145B ->149B -0.12461

Excited State 9: 2.519-A 3.3885 eV 365.90 nm f=0.1515 <S**2>=1.337
142A ->150A 0.10043
143A ->151A -0.17653
144A ->150A 0.14758
147A ->149A 0.75767
141B ->147B -0.29290
142B ->149B 0.12072
143B ->151B -0.14086
144B ->149B -0.11079
144B ->150B -0.10186
145B ->147B -0.28555
145B ->148B -0.11114

Excited State 10: 3.099-A 3.6574 eV 338.99 nm f=0.0000 <S**2>=2.150
142A ->148A -0.19931
142A ->151A 0.10238
143A ->150A -0.23216
144A ->151A 0.21517
145A ->149A 0.19130
145A ->150A -0.11991
146A ->152A 0.27302
147A ->156A 0.11418
139B ->147B 0.33494
140B ->147B 0.39658
142B ->148B 0.18729
142B ->151B 0.11147
143B ->150B 0.21609
144B ->148B -0.11191
144B ->151B 0.19363
145B ->149B -0.19780
145B ->150B 0.11135
146B ->152B -0.25264

F_2PyBTM (UB3LYP/6-31G(d))

121A is SOMO.

Excited State 1:	2.145-A	2.6088 eV	475.26 nm	f=0.0065	<S**2>=0.900
121A ->123A	0.13726				
119B ->121B	0.42202				
120B ->121B	0.86425				
Excited State 2:	2.157-A	2.6811 eV	462.44 nm	f=0.0284	<S**2>=0.913
121A ->123A	0.17467				
117B ->121B	-0.20725				
119B ->121B	0.81345				
120B ->121B	-0.44578				
Excited State 3:	2.173-A	2.7200 eV	455.83 nm	f=0.0095	<S**2>=0.930
121A ->122A	-0.25413				
114B ->121B	-0.10696				
116B ->121B	0.44110				
118B ->121B	0.81297				
Excited State 4:	2.141-A	2.8846 eV	429.81 nm	f=0.0076	<S**2>=0.896
121A ->122A	-0.25313				
116B ->121B	0.76834				
118B ->121B	-0.54091				
Excited State 5:	2.110-A	2.9206 eV	424.52 nm	f=0.0023	<S**2>=0.863
115B ->121B	0.31982				
117B ->121B	0.89735				
119B ->121B	0.21382				
Excited State 6:	2.258-A	2.9386 eV	421.91 nm	f=0.0046	<S**2>=1.025
121A ->123A	0.20056				
115B ->121B	0.87089				
115B ->123B	0.15307				
117B ->121B	-0.31528				
119B ->123B	-0.10813				
Excited State 7:	2.258-A	3.3047 eV	375.17 nm	f=0.0236	<S**2>=1.025
116A ->122A	0.16536				
121A ->122A	0.49575				
121A ->129A	-0.22385				
106B ->121B	-0.11236				

114B ->121B 0.67724
116B ->121B 0.27573
120B ->128B -0.12583

Excited State 8: 2.532-A 3.3859 eV 366.18 nm f=0.1338 <S**2>=1.353
117A ->125A 0.14716
118A ->122A 0.10531
119A ->124A 0.18170
121A ->123A 0.76574
115B ->121B -0.22182
116B ->122B 0.15782
117B ->121B 0.13126
117B ->125B -0.13573
118B ->122B 0.12274
118B ->124B 0.12688
119B ->121B -0.28278
119B ->123B -0.12782

Excited State 9: 2.875-A 3.5235 eV 351.88 nm f=0.1091 <S**2>=1.817
116A ->122A -0.14662
117A ->123A -0.13218
117A ->124A -0.18289
118A ->123A 0.10173
118A ->124A -0.17671
119A ->125A -0.25078
120A ->123A -0.20413
121A ->122A 0.52037
121A ->129A 0.15863
114B ->121B -0.29691
116B ->121B 0.33527
116B ->123B 0.16581
117B ->122B 0.11030
117B ->124B 0.18864
118B ->125B -0.20749
119B ->122B -0.23390
119B ->124B 0.13407

Excited State 10: 2.262-A 3.7188 eV 333.40 nm f=0.0079 <S**2>=1.029
118A ->125A -0.10133
121A ->123A 0.20361
121A ->124A 0.92845
116B ->124B 0.12858
117B ->121B 0.10049

119B ->125B 0.11141

Br_2PyBTM (UM06/6-31G(d))

147A is SOMO.

Excited State 1: 2.298-A 2.6146 eV 474.21 nm f=0.0154 <S**2>=1.070
147A ->149A 0.27454
145B ->147B 0.51266
146B ->147B 0.73262
This state for optimization and/or second-order correction.
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 2.379-A 2.7561 eV 449.86 nm f=0.0044 <S**2>=1.164
145A ->149A 0.12149
147A ->148A 0.31761
147A ->156A 0.10494
140B ->148B 0.10378
142B ->147B -0.48547
144B ->147B 0.70107
145B ->149B -0.10494

Excited State 3: 2.224-A 2.8343 eV 437.45 nm f=0.0103 <S**2>=0.986
146A ->148A 0.12097
147A ->149A 0.17556
145B ->147B 0.69688
146B ->147B -0.63208
146B ->148B -0.13555

Excited State 4: 2.263-A 3.0485 eV 406.71 nm f=0.0006 <S**2>=1.030
147A ->148A -0.15730
147A ->151A -0.10561
147A ->156A -0.10474
140B ->147B 0.22311
142B ->147B 0.65956
142B ->148B -0.10118
144B ->147B 0.60097

Excited State 5: 2.161-A 3.0677 eV 404.16 nm f=0.0058 <S**2>=0.918
147A ->149A -0.13446
147A ->150A -0.13761
143B ->147B 0.92940

144B ->149B 0.11308
145B ->147B 0.21187

Excited State 6: 2.638-A 3.1466 eV 394.02 nm f=0.0003 <S**2>=1.489
142A ->148A 0.18624
144A ->148A -0.14672
145A ->152A 0.12154
146A ->152A -0.17236
147A ->148A 0.22793
147A ->156A -0.15905
129B ->147B 0.10194
137B ->147B -0.10104
140B ->147B 0.69090
140B ->148B 0.12915
142B ->147B -0.14720
144B ->147B -0.24715
144B ->148B 0.13762
145B ->152B -0.11007
146B ->150B 0.10383
146B ->152B 0.18619

Excited State 7: 2.472-A 3.2833 eV 377.62 nm f=0.0266 <S**2>=1.277
143A ->151A 0.12954
145A ->148A 0.11197
147A ->149A 0.38710
141B ->147B 0.69722
141B ->148B 0.18708
143B ->147B 0.18848
143B ->151B -0.11091
145B ->147B -0.32051
145B ->148B -0.14668
146B ->147B -0.10204
146B ->148B -0.10505

Excited State 8: 2.454-A 3.3706 eV 367.84 nm f=0.0907 <S**2>=1.255
143A ->150A -0.14368
144A ->151A -0.14828
145A ->149A 0.11570
147A ->148A 0.68972
140B ->147B -0.12534
142B ->147B 0.49880
143B ->150B 0.10060
144B ->147B -0.19111

145B ->149B -0.13198

Excited State 9: 2.500-A 3.4372 eV 360.71 nm f=0.1238 <S**2>=1.312
142A ->150A -0.10313
143A ->151A -0.17652
144A ->150A -0.13891
147A ->149A -0.51172
141B ->147B 0.62472
141B ->148B 0.19092
143B ->147B -0.13752
143B ->151B 0.13561
145B ->147B 0.25638
146B ->147B 0.11952

Excited State 10: 2.924-A 3.6758 eV 337.30 nm f=0.0048 <S**2>=1.887
142A ->148A -0.15741
142A ->151A -0.11484
143A ->150A -0.22119
144A ->151A -0.21324
145A ->149A 0.11652
145A ->150A -0.16120
145A ->152A -0.11642
146A ->152A 0.24647
147A ->148A -0.21633
140B ->147B 0.59810
142B ->148B 0.14369
142B ->151B 0.12997
143B ->150B 0.19893
144B ->151B 0.18474
145B ->149B -0.12251
145B ->150B 0.14853
146B ->149B -0.10364
146B ->152B -0.22071

F_2PyBTM (UM06/6-31G(d))

121A is SOMO.

Excited State 1: 2.325-A 2.6801 eV 462.61 nm f=0.0184 <S**2>=1.102
121A ->123A -0.29407
116B ->122B 0.10696
117B ->121B 0.11555
119B ->121B -0.41940

120B ->121B 0.76885

Excited State 2: 2.349-A 2.7791 eV 446.13 nm f=0.0078 <S**2>=1.129
120A ->123A 0.15299
121A ->122A 0.33384
114B ->121B 0.11821
116B ->121B -0.52319
118B ->121B 0.66923
120B ->122B -0.11437

Excited State 3: 2.183-A 2.8233 eV 439.15 nm f=0.0102 <S**2>=0.942
117B ->121B -0.21129
119B ->121B 0.77385
120B ->121B 0.52632
120B ->123B 0.11596

Excited State 4: 2.186-A 3.0437 eV 407.35 nm f=0.0013 <S**2>=0.945
121A ->122A -0.22153
116B ->121B 0.63092
118B ->121B 0.69224

Excited State 5: 2.158-A 3.0673 eV 404.21 nm f=0.0035 <S**2>=0.914
121A ->123A -0.14964
121A ->124A -0.12200
117B ->121B 0.89427
118B ->122B -0.11895
119B ->121B 0.32106

Excited State 6: 2.338-A 3.1298 eV 396.15 nm f=0.0019 <S**2>=1.116
121A ->123A 0.20343
115B ->121B 0.87170
115B ->123B 0.22725
117B ->121B 0.18430
119B ->121B -0.10883
119B ->123B -0.10086
120B ->123B 0.10525

Excited State 7: 2.608-A 3.3056 eV 375.07 nm f=0.0020 <S**2>=1.451
116A ->122A 0.23153
118A ->125A -0.11723
119A ->127A 0.11142
120A ->123A -0.16789
121A ->122A 0.31016

121A ->129A -0.23996
106B ->121B -0.12849
110B ->121B 0.11058
114B ->121B 0.68359
114B ->123B 0.10869
116B ->121B 0.10016
116B ->123B -0.15409
118B ->125B 0.12802
119B ->128B -0.10426
120B ->122B 0.10207
120B ->128B -0.12959

Excited State 8: 2.573-A 3.4072 eV 363.89 nm f=0.1473 <S**2>=1.404
117A ->125A -0.16497
118A ->124A 0.19705
119A ->125A -0.12344
120A ->122A 0.11333
120A ->129A 0.10208
121A ->123A 0.62052
121A ->124A -0.11940
115B ->121B -0.35245
116B ->122B -0.12654
116B ->124B -0.10876
117B ->121B 0.21599
117B ->125B 0.14686
118B ->122B 0.12212
118B ->124B -0.12865
119B ->121B -0.24979
120B ->121B 0.27991

Excited State 9: 2.726-A 3.5023 eV 354.00 nm f=0.1149 <S**2>=1.608
117A ->123A -0.12934
117A ->124A -0.18534
118A ->125A 0.24696
119A ->124A -0.16588
120A ->123A 0.18975
121A ->122A 0.53384
116B ->121B 0.52012
116B ->123B 0.11180
117B ->122B -0.11811
117B ->124B 0.16554
118B ->121B -0.16366
118B ->125B -0.18653

119B ->122B 0.11243
119B ->124B 0.14345
120B ->122B -0.17007

Excited State 10: 2.366-A 3.7814 eV 327.88 nm f=0.0148 <S**2>=1.150
120A ->125A 0.14852
121A ->123A 0.30564
121A ->124A 0.86367
116B ->124B 0.16048
117B ->121B 0.14892
119B ->125B -0.11625